J. Elementol. 2010, 15(1): 19–29

DESORPTION OF PHOSPHATE (V) IONS FROM BROWN SOIL

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Abstract

The objective of the study was to determine, under laboratory conditions, the rate of phosphate (V) ions leaching down brown soil horizons under the influence of redistilled water of pH 6.2. Laboratory tests were conducted to determine the effect of mineral and organic fertilization on phosphate (V) ion concentrations in brown soil horizons before and after extraction with water. The content of desorbed PO_4^{3-} ions was determined in percolating water samples. The results indicate that the quantity of desorbed phosphate (V) ions was affected by the type and rate of fertilization as well as by the dose of the applied solvent. The highest desorption of phosphate (V) ions from the brown soil profile was reported in the treatment fertilized with manure + PK, while the lowest desorption was observed in the plot fertilized with NPK. The maximum desorption of phosphate (V) ions was noted in soil layers at the depths of 0-25 cm and 26-50 cm. In all filtrate samples, PO_4^{3-} values significantly exceeded the minimum quantity required to initiate eutrophication. The highest content of phosphate (V) ions, at 64.8 mg $PO_4^{3-} \cdot kg^{-1}$ soil, was determined in percolating water from the treatment fertilized with slurry rate II (123.8 $t \cdot ha^{-1}$). Percolating water samples collected in the non-fertilized (control) plot were least abundant in phosphate (V) ions (21.7 mg $PO_4^{3-} \cdot kg^{-1}$ soil).

Key words: phosphorus, leaching, fertilization, soil.

WYMYWANIE JONÓW FOSFORANOWYCH (V) Z GLEBY BRUNATNEJ

Abstrakt

Celem pracy by³o zbadanie, w warunkach laboratoryjnych, intensywnoœci przemieszczania siê jonów fosforanowych (V) w g³¹b poszczególnych warstw profilu gleby brunatnej pod wp³ywem wody redestylowanej o pH=6,2. Zakres badañ obejmowa³ okreœlenie wp³ywu nawo¿enia mineralno-organicznego na zawartoœæ jonów fosforanowych (V) w poszczegól-

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nych warstwach gleby brunatnej przed i po ekstrakcji wod¹. Oznaczono tak¿e iloœæ zdesorbowanych jonów PO_4^{3-} w zebranych wodach przesi¹kowych. Stwierdzono, ¿e iloœæ zdesorbowanych jonów fosforanowych (V) zale¿a³a od rodzaju i dawki nawo¿enia oraz iloœci zastosowanego rozpuszczalnika. Najwiêksz¹ desorpcjê jonów fosforanowych (V) z profilu gleby brunatnej uzyskano z obiektu nawo¿onego obornikiem + PK, natomiast najmniejsz¹ z obiektu nawo¿onego NPK. Maksimum desorpcji jonów fosforanowych (V) stwierdzono z warstw 0-25 cm i 26-50 cm. We wszystkich zebranych przes¹czach oznaczone wartoœci PO_4^{3-} przekracza³y znacznie minimaln¹ iloœæ potrzebn¹ do zapocz¹tkowania eutrofizacji. Najwiêksz¹ zawartoœæ jonów fosforanowych (V), wynosz¹c¹ 64,8 mg $PO_4^{3-} \cdot kg^{-1}$ gleby, stwierdzono w wodach przesi¹kowych pochodz¹cych z obiektu nawo¿onego II dawk¹ gnojowicy (123,8 $t \cdot ha^{-1}$). Najmniejsz¹ iloœæ analizowanych jonów (21,7 mg $PO_4^{3-} \cdot kg^{-1}$gleby) oznaczono w wodach przesi¹kowych zebranych z obiektu nie nawo¿onego (kontrolnego).

S³owa kluczowe: fosfor, wymywanie, nawo¿enie, gleba.

INTRODUCTION

The rapid growth in production and the mass scale application of phosphorus fertilizers in the 1960s and 1980s resulted in vast accumulation of phosphorus in soil and its migration into the environment (Sapek 2001, Gassner, Grzebisz 2003). The problem of excessive phosphorus deposition is also encountered in Poland, and it is of economic importance as it deteriorates the quality of water resources, which are already scant. Despite the high cost of water protection projects, water contamination with phosphorus was not abated in the following years (Koc, Skwierawski 2003). A detailed study investigating the significance of the sources of phosphorus migration was carried out in the European Union in the early 1990s, and it revealed that more than 50% of phosphorus found in surface waters of the EU countries originated from farming (Grzebisz, Potarzycki 2003). Surface leaching is the main factor responsible for phosphorus migration to surface water. Leaching down through the soil profile is also an important contributor to this process, in particular in sandy soils and substrates with large soil macropores (McGechan 2003). For this reason, any convenient and economically viable method of long-term fertilization requires effective phosphorus immobilization to ensure that the nutrient requirements of crops are met but phosphorus desorption from the soil under the influence of atmospheric precipitation is prevented. The above is also an important consideration in the prevention of groundwater eutrophication (Moskal et al. 1999, Sapek, Urbaniak 2001).

The objective of the study was to determine, in laboratory conditions, the rate of phosphate ion (V) leaching down through brown soil horizons under the influence of redistilled water, and to estimate the effect of varied mineral and organic fertilization on the leaching of PO_4^{3-} ions away from brown soil.

MATERIALS AND METHODS

Soil samples were collected after the 2003 harvest from experimental plots established in 1972 by the Chair of Environmental Chemistry, at the Experimental Station in Tomaszkowo near Olsztyn. They comprised brown soil developed from slightly loamy sand, of good rye complex and quality class IVb. The rates of organic fertilizers were set based on the total nitrogen and organic carbon content determined every year prior to their application. Three fertilization systems were compared in the experiment: organic, mineral and combined organic and mineral.

Eight fertilizer combinations were applied in the study: no fertilization, slurry rate I, slurry rate I + PK, slurry rate II, slurry rate II + PK, manure, manure + PK, NPK. Pig manure and slurry were used as organic fertilizers. Slurry was administered at two rates: rate I – equivalent to the manure rate as regards the amount of nitrogen introduced into the soil, and rate II – equivalent to the manure rate as regards the amount of carbon introduced into the soil. Organic fertilizers were supplemented with mineral (phosphorus and potassium) fertilizers at half the rate applied in the treatment fertilized with NPK. The nitrogen content of mineral fertilizers corresponded to the nitrogen content of manure and slurry rate I. The levels of phosphorus and potassium fertilization were adjusted so as to meet the nutrient requirements of particular crop species (S¥DEJ 2000). Soil texture (size fractions) was determined by the method suggested by Pruszyñski (Table 1).

Table 1

Soil size fractions according to Pruszyński's method

Brown soil							
Soil horizon (cm)	fraction group*	percentage content of soil fractions, in mm					
		1.0-0.1	0.1-0.05	0.05-0.02	0.02-0.005	0.005-0.002	< 0.002
0-25	sls	55	32	6	3	3	1
26-50	lss	50	33	10	3	2	2
51-75	ssl	45	40	9	2	3	1
76-100	mhl	44	39	9	3	2	3

*Explanatioms: sls – slightly loamy sand, lss – loose silty sand, ssl – silty sandy loam, mhl – medium-heavy loam

Because of the low mobility of phosphate (V) ions, their migration into the soil profile to a depth of 1 m was investigated in this study. Soil samples were collected from four horizons: 0-25 cm, 26-50 cm, 51-75 cm and 76--100 cm. The samples were air-dried, purified of plant debris, sifted through a 1 mm mesh sieve and placed in glass columns 93 cm high and 5 cm in internal diameter, with a water-permeable layer of silica sinter at the bottom. The soil's original structure was preserved while filling the columns to create a natural testing environment. Every column was filled with layers of soil to a height of 80 cm (20 cm for every horizon: 0-25; 26-50, 51-75 and 76-100). The weight of soil samples was 1,760 g on average in each column. Redistilled water 6.2 in pH, stored in a corked bottle with CaO, was passed through the soil layers in columns in order to moisten them. The water had similar properties to rain water. On successive days of the experiment, filtrate samples (200 ml on average) were collected in a controlled environment and analyzed by molybdate and vanadate photoelectric colorimetry to determine phosphate (V) ion concentrations. The average total volume of percolating water samples from each column was 6.5 dm^3. The samples were preserved with toluene and refrigerated until analysis. The content of phosphate (V) ions was determined by the Egner-Rhiem method in every soil layer, for every fertilization system, before and after extraction with water.

The results were processed statistically by correlation analysis, linear regression analysis and the relevant parametric significance tests. The significance of correlations was determined with the use of Student's t-test. Correlation coefficients were compared with a normal distribution test. Regression functions were compared by Fisher F-test. The formulated hypotheses were verified at a significance level of α=0.05. Statistical calculations and data presentations were performed with Statistica PL and Excel applications.

RESULTS AND DISCUSSION

The effect of multi-year fertilization on phosphate (V) ion concentrations in each brown soil horizon is presented in Figure 1. The observed values were compared following desorption with water with pH of 6.2 (Fig. 1b). Among the treatments with equal amounts of nitrogen introduced to soil, the highest levels of phosphate (V) ions were noticed for the treatment fertilized with manure. The reported values were 1.5-fold lower than in the NPK-fertilized plot. The highest accumulation of the analyzed ions in the manure-fertilized treatment was observed in the ploughed layer (482 mg $PO_4^{3-} \cdot kg^{-1}$ soil) and in the subsoil horizon (442 mg $PO_4^{3-} \cdot kg^{-1}$ soil). In the plots fertilized with slurry rate I and NPK, the highest phosphate (V) ion content was observed in the ploughed layer (436.8 and 403 mg $PO_4^{3-} \cdot kg^{-1}$ soil, respectively). Similar results were reported by Grzebisz et al. (1992), Str¥czyñska (1998), Koper et al. (2002), Wac£awowicz (2002), Sienkiewicz (2003), Zimny, Kuc (2005), Kalebasa et al. (2005) and Toor et al. (2005). The passage of water caused the highest desorption of PO_4^{3-} ions in the treatment ferti-

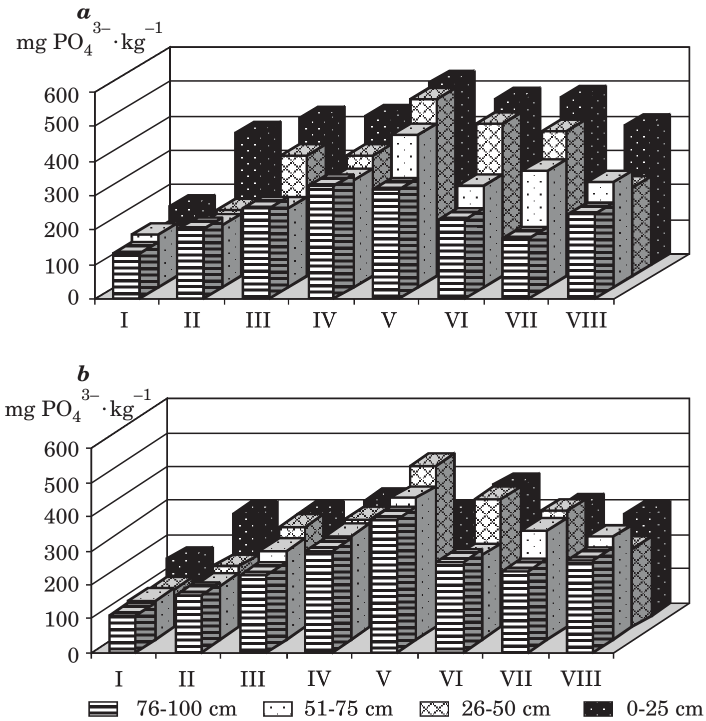

Fig. 1. Phosphate (V) ion concentrations in brown soil: *a* – before desorption; *b* – after desorption with water, I – control, II – slurry rate I, III – slurry rate I + PK, IV – slurry rate II, V – slurry rate II +PK, VI – manure, VII – manure + PK, VIII – NPK

lized with slurry rate I (213 mg $PO_4^{3-} \cdot kg^{-1}$ soil), corresponding to 21% of the total phosphate (V) ion content of the entire soil profile. The analyzed ions were leached out from each horizon, mostly from the ploughed layer (32.52%) and the 76-100 cm horizon (17.76%) – Table 2. In the remaining plots, the quantity of phosphate (V) ions desorbed from the entire soil profile was 12% in the manure-fertilized treatment and 9% in the NPK-fertilized treatment. In the plot with mineral fertilization, the highest quantity of phosphate (V) ions was leached out from the ploughed layer and from the subsoil horizon. Ion sorption in the 76-100 cm horizon reached 10.44% PO_4^{3-}.

The results indicate that smaller quantities of phosphate (V) ions were leached out by distilled water from brown soil with mineral fertilization (NPK), compared to plots fertilized with slurry rate I and manure. The observations made by other authors confirm that the rate of translocation into deeper horizons of the soil profile is higher in respect of phosphate (V) ions from organic than from mineral fertilizers (Witthon et al. 1991, Moskal et al. 1999, Frossard et al. 2000, Hooda et al. 2001, Sapek, Urbaniak 2001, Toor et al. 2004, Marshall, Laboski 2006).

Table 2

Phosphate (V) ion desorption from brown soil fertilized with slurry rate I, slurry rate I + PK, slurry rate II, slurry rate II + PK, manure, manure + PK

Soil horizon (cm)	Control	Slurry rate I	Slurry rate I + PK	Slurry rate II	Slurry rate II + PK	Manure	Manure + PK	NPK
		PO_4^{3-} desorption (%)						
0-25	33.33	32.52	30.82	22.67	38.03	21.11	34.35	26.58
26-50	13.24*	6.99	15.65	8.85	7.83	14.55	18.53	10.47
51-75	10.89*	12.03	15.98*	2.15	6.34	15.91	5.14	0.44
76-100	-	17.76	13.27	10.16	23.31*	16.47*	36.92*	10.44*

*PO_4^{3-} sorption (%)

The treatments fertilized with slurry rate II and manure, equivalent in terms of the amount of carbon introduced into soil, were characterized by a similar content of phosphate (V) ions throughout the entire soil profile, which reached 355 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the plot fertilized with slurry rate II and 361 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the manure-fertilized plot. In comparison with soil fertilized with slurry rate II, the concentrations of the analyzed ions in the manure-fertilized treatment were higher by 50.9 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the ploughed layer and by 93.8 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the subsoil horizon. Soil fertilized with slurry rate II contained more phosphate (V) ions than the manure-fertilized plot, by 17 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the 51-75 cm horizon and by 101.8 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the deepest (76-100 cm) horizon. This suggests that the migration of phosphate (V) ions into the deepest horizon below the depth of 100 cm is higher in soils fertilized with slurry rate II than in manure-fertilized soils. The above could be attributed to the fact that slurry has an average 97% water content. Similar results were reported by Koper (1994) and Vadas (2006). The use of distilled water resulted in the desorption of phosphate (V) ions in the first three horizons of soil fertilized with manure, while in the deepest horizon, ion sorption reached 37 mg $PO_4^{3-} \cdot kg^{-1}$ soil (16.47%). PO_4^{3-} ions were leached out from all horizons in plots fertilized with slurry rate II.

Slurry rate II increased phosphate (V) ion concentrations in the entire brown soil profile by an average of 30% in comparison with treatments fertilized with slurry rate I. In the ploughed layer, the quantity of phosphate (V) ions reached 436 mg $PO_4^{3-} \cdot kg^{-1}$ soil after the application of slurry rate I and 431 mg $PO_4^{3-} \cdot kg^{-1}$ soil after the application of slurry rate II. In the subsoil fertilized with slurry rate II, the content of the analyzed ions increased by 156 mg $PO_4^{3-} \cdot kg^{-1}$ soil. In the two remaining horizons (51-75 cm and 76-100 cm), phosphate (V) ion levels increased by 130 mg $PO_4^{3-} \cdot kg^{-1}$ soil on average in comparison with plots fertilized with slurry rate I.

An average of 11% phosphate (V) ions from the entire soil profile was desorbed with distilled water in the plot fertilized with slurry rate II, and 21% in the treatment fertilized with slurry rate I. PO_4^{3-} desorption in the 51-75 cm horizon fertilized with slurry rate II was five-fold lower than in the same horizon fertilized with slurry rate I.

The application of supplementary phosphorus-potassium fertilizers at half the NPK rate increased phosphate (V) ion concentrations throughout the entire brown soil profile fertilized with slurry rate I and II, by 64 and 81.7 mg $PO_4^{3-} \cdot kg^{-1}$ respectively. In soil fertilized with slurry rate I, supplementary PK fertilization increased the levels of phosphate (V) ions by 159 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the 26-50 cm horizon, by 48 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the 51-75 cm horizon, and by 58 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the 76-100 cm horizon. In soil fertilized with slurry rate II, PK supplementation increased phosphate (V) ion concentrations in the above three horizons by 44, 164.8 and 131 mg $PO_4^{3-} \cdot kg^{-1}$ soil, respectively. PK supplementary fertilization did not increase the PO_4^{3-} content of manure-fertilized brown soil.

The concentrations of phosphate (V) ions in percolating water samples from each brown soil plot are presented in Figure 2. These data indicate that the average content of phosphate (V) ions in the total volume of filtrates (6.5 dm^3) collected in fertilized treatments after the use of water was twice as high as in the filtrate from the control treatment. The phosphate (V) ion content of filtrate samples obtained from fertilized plots increased with the quantity of water used. The above points to the possibility of increased PO_4^{3-} desorption in fertilized soil even when water volume exceeds 6.5 dm^3.

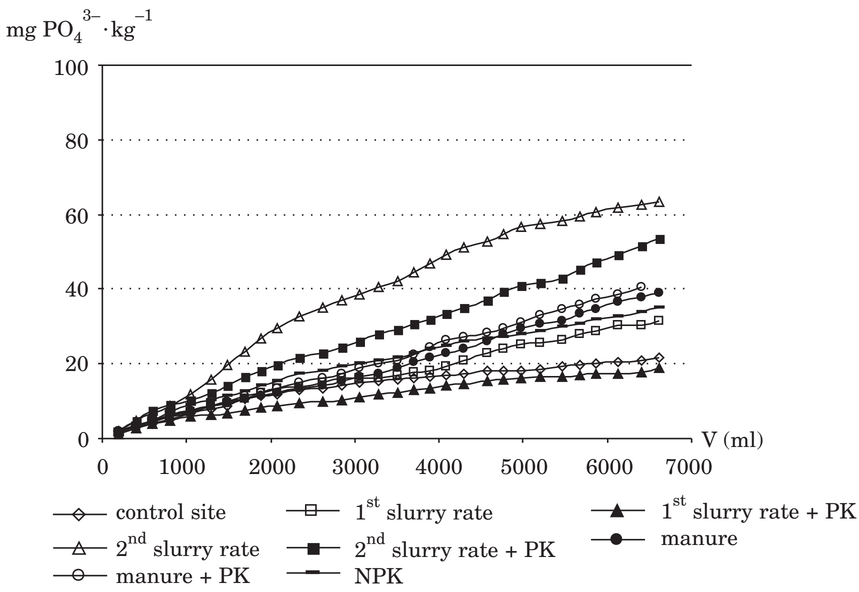

Fig. 2. Phosphate (V) ion concentrations in filtrate samples from brown soil

Table 3

The effect of soil horizon (measurement depth) on phosphate ion concentrations before and after desorption with water
Evaluation of correlations (correlation analysis and linear regression analysis) in experimental plots

Plot	Collection	Parameter		Correlation		Regression function $y = a + b \cdot x$	
		x	s	r	p	a	b
I control	before	314.23	67.11	-0.713	0.047	349.55	-1.583
	water	295.47	11.28	0.208	0.621	291.53	0.078
II 1st slurry rate	before	252.59	114.14	-0.753	0.031	396.80	-2.842
	water	199.33	59.51	-0.816	0.014	280.78	-1.605
III 1st slurry rate + PK	before	316.58	83.19	-0.886	0.003	440.21	-2.436
	water	270.35	29.96	-0.932	0.001	317.21	-0.923
IV 2nd slurry rate	before	355.44	48.91	-0.840	0.009	424.36	-1.358
	water	313.23	15.03	-0.992	<0.001	338.25	-0.493
V 2nd slurry rate + PK	before	437.18	79.18	-0.822	0.012	546.41	-2.152
	water	393.29	68.79	0.404	0.320	346.58	0.920
VI manure	before	361.80	111.43	-0.976	<0.001	544.31	-3.596
	water	317.92	65.93	-0.861	0.006	413.19	-1.877
VII manure + PK	before	354.10	123.83	-0.972	<0.001	556.13	-3.981
	water	304.85	42.13	-0.724	0.042	356.04	-1.009
VIII NPK	before	301.50	67.14	-0.773	0.024	388.63	-1.717
	water	274.03	30.64	-0.038	0.929	275.97	-0.038

The highest content of phosphate (V) ions, 64.8 mg $PO_4^{3-} \cdot kg^{-1}$ soil, was determined in the total volume of percolating water (6.5 dm^3) samples collected in the plot fertilized with slurry rate II. The lowest concentrations of the analyzed ions (21.7 mg $PO_4^{3-} \cdot kg^{-1}$ soil) were observed in the control treatment. In filtrate samples (total volume of 6.3 dm^3) collected from plots fertilized with manure, slurry rate I and mineral fertilizers, equivalent in terms of the amount of nitrogen introduced into soil, the highest concentrations of phosphate (V) ions were desorbed in manure-fertilized soil (36.5 mg $PO_4^{3-} \cdot kg^{-1}$ soil), followed by treatments fertilized with NPK (33 mg $PO_4^{3-} \cdot kg^{-1}$ soil) and slurry rate I (30 mg $PO_4^{3-} \cdot kg^{-1}$ soil). The desorption of phosphate (V) ions reached 50.8 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the NPK-fertilized plot, and 41 mg $PO_4^{3-} \cdot kg^{-1}$ soil in the plot fertilized with slurry rate I. In treatments fertilized with slurry rate II and manure, equivalent with respect to the amount of carbon introduced into soil, the highest phosphate

Table 4

Phosphate ion concentrations in filtrate samples after desorption with water
Evaluation of correlations (correlation analysis) in experimental plots

Plot	Water	
	r	*p*
I = control	0.968	<0.001
II = 1st slurry rate	0.995	<0.001
III = 1st slurry rate + PK	0.992	<0.001
IV = 2nd slurry rate	0.988	<0.001
V = 2nd slurry rate + PK	0.999	<0.001
VI = manure	0.996	<0.001
VII = manure + PK	0.998	<0.001
VIII = NPK	0.993	<0.001

*if $p \le 0.05$ ($p \le 0.10$), then regression functions are not parallel

(V) ion concentrations were noticed in filtrate samples from the plot fertilized with slurry rate II, being 60% higher in comparison with the manure-fertilized treatment. The content of PO_4^{3-} ions in filtrate samples from the plots fertilized with manure and with slurry rate II increased with the amount of water used (pH=6.2).

The content of phosphate (V) ions determined in the total volume of filtrate (6.5 dm^3 on average) samples collected in plots fertilized with two different slurry rates was on average twice as high in the plot fertilized with slurry rate II as in the treatment fertilized with slurry rate I. Phosphate (V) ion concentrations in filtrate samples collected from soil fertilized with slurry rate II increased along with an increase in the volume of water to an average of 5 dm^3. The above points to the continual activation and leaching out of PO_4^{3-} ions from plots fertilized with slurry rate II. The content of phosphate (V) ions was lower in filtrate samples collected in the plot with phosphorus-potassium fertilization.

The results, including mean (x) and standard deviation (s) values, obtained for fertilized brown soil plots before and after desorption with water are presented in Table 3. The table presents the correlations (r) between phosphate (V) ion concentrations in each layer and the soil horizon (measurement depth), and the significance (p) of the determined correlations. The parameters of a simple regression function were also determined. As shown by the presented data, most of the correlations are statistically significant ($p \le 0.05$). Table 4 presents the correlations between phosphate (V) ion concentrations in filtrate samples after desorption with water and the quantity of water used. All correlation coefficients were found to be statistically significant.

CONCLUSIONS

1. Long-term mineral and organic fertilization leads to increased accumulation of phosphate (V) ions in brown soil. The highest ion concentrations were determined in plots fertilized with slurry rate II + PK, manure, and manure + PK.

2. The highest desorption of phosphate (V) ions with water was noticed in brown soil fertilized with manure + PK, and the lowest – in the NPK-fertilized treatment.

3. The maximum desorption of phosphate (V) ions with water was observed in soil horizons at the depths of 0-25 cm and 26-50 cm.

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